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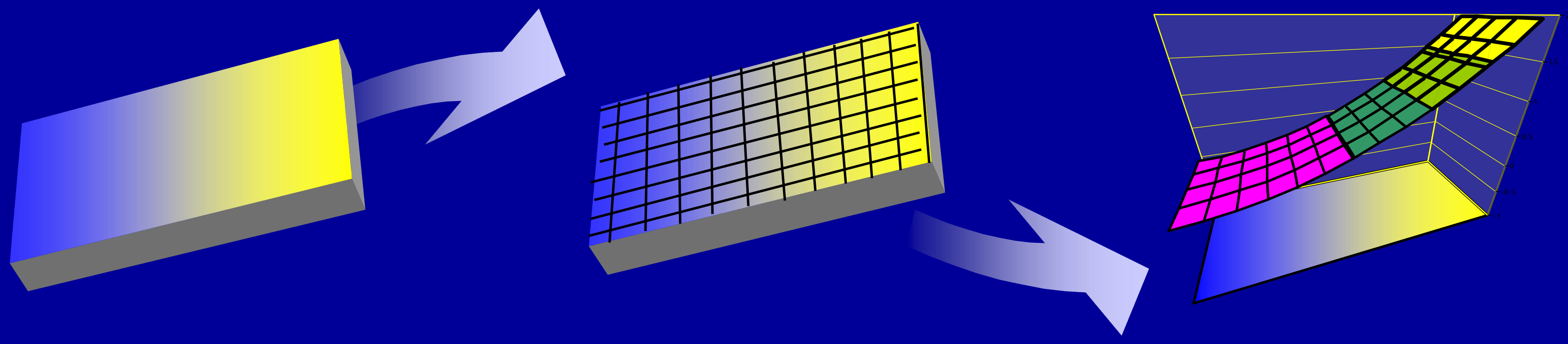
Gradient Library Calibration

Recommended practices for gradient combi techniques…

Michael Fasolka, Amit Sehgal, Kathryn Beers



NCMC-1: April 26, 2002

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Calibration

Calibration of Library Variable Space

Thickness, Composition, Surface Energy, etc.

Instrumentation Calibration

Temperature stage, Translation Stages

Resolution, Tolerance and Uncertainty of Measurements

Design

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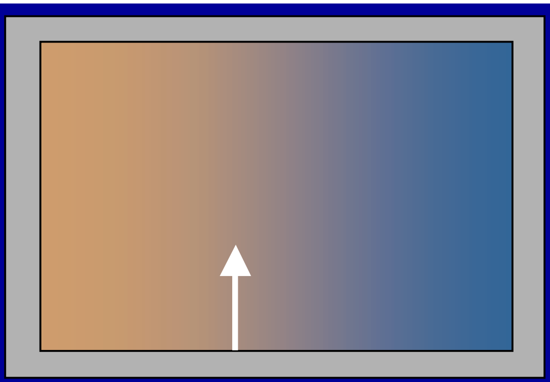
Why is Library Calibration Necessary?

The Cartoon Gradient



Linear gradient

- one slope
- even along “y”

Known dimension and orientation

Known scope

Defect Free

Reality

Non-linear gradient

- Variable slopes in x and y

Arbitrary orientation

Scope approximate

Defects Present

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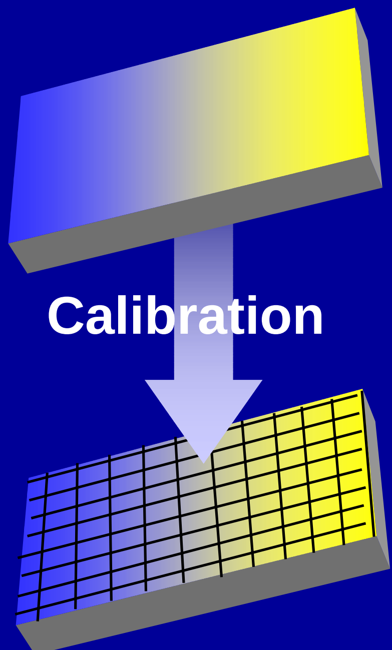
Library Calibration:

What is needed before a gradient library is useful for combinatorial research?



- Spatial reference grid
  - Mesh of calibration measurements
- Flaw/defect criteria met
- Library scope overlaps known phenomenon
  - “Built-in” standard
- Scope and tolerance of library known
  - Evaluation of uncertainty

Practices for processing combi gradient libraries so they can be “handled” like discrete combi libraries

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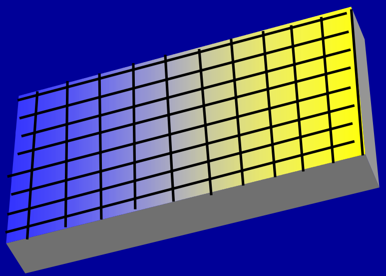
Spatial Reference Grids (SRG):

Define the sample space with respect to a reference or “fiduciary” marking system



Spatial Reference Grids Enable:

- Organization/Automation of sample measurements
- Definition of non-linear gradients (almost all!).
- Alignment/Registry of multiple gradients
- Definition and measurement of gradient steepness
- Interpolation: “zooming in”, “isobars”
- Library transfer (e.g. to another substrate)

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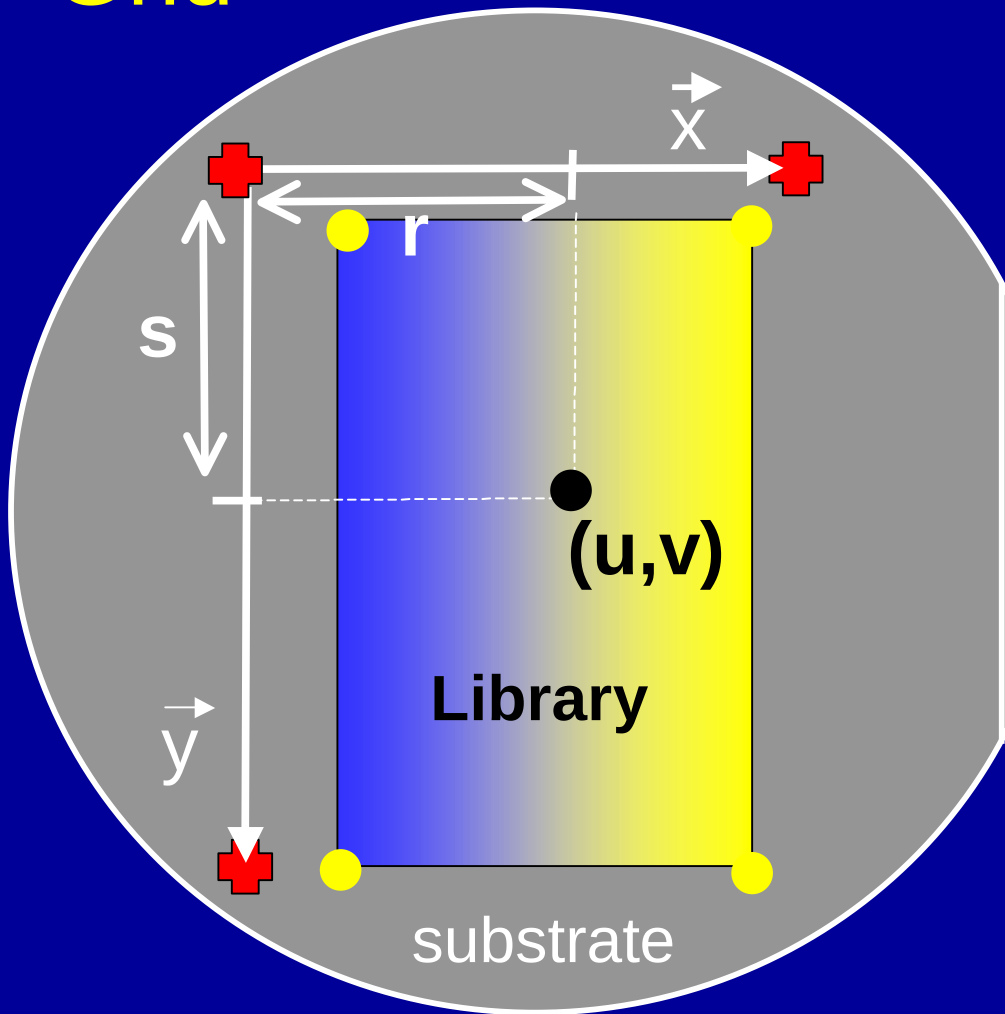
Elements of a Spatial Reference Grid



3-Point Fiduciary Mark System

Reference Vectors $\vec{x}$ & $\vec{y}$

Coordinate System

$$(u,v) = \left(r\frac{\vec{x}}{|\vec{x}|} , s\frac{\vec{y}}{|\vec{y}|} \right)$$

Library boundaries defined in terms of **(u,v)**

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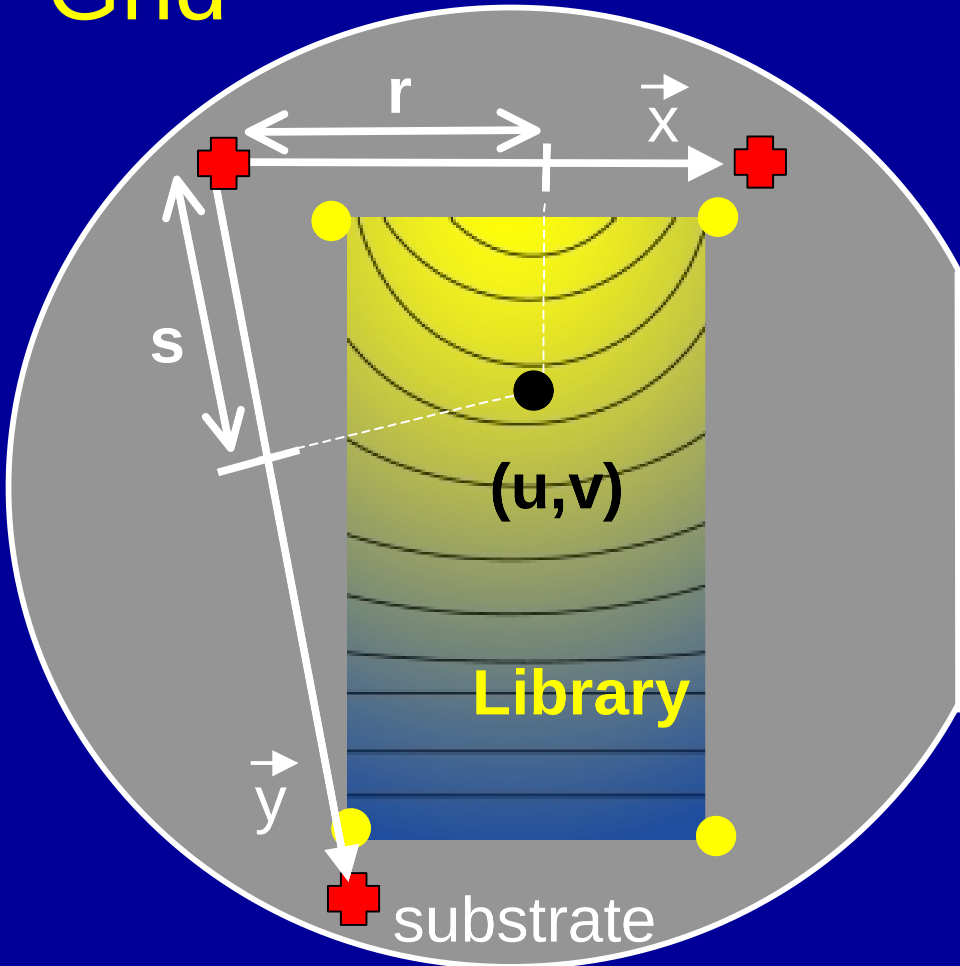
Elements of a Spatial Reference Grid



- Reference vector analysis accommodates non-orthogonal fiduciary systems
- The SRG defines the points onto which a mesh of calibration measurements are built. This mesh defines the library variable space.

Library boundaries

Fiduciary Marks

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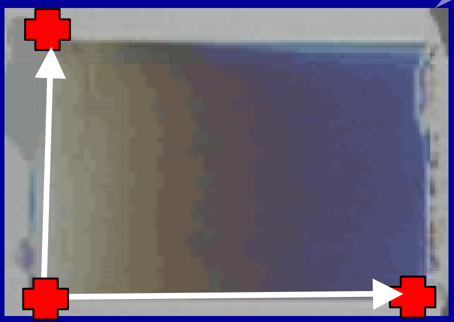
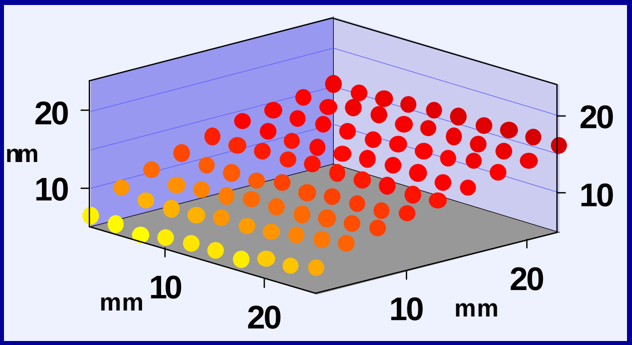
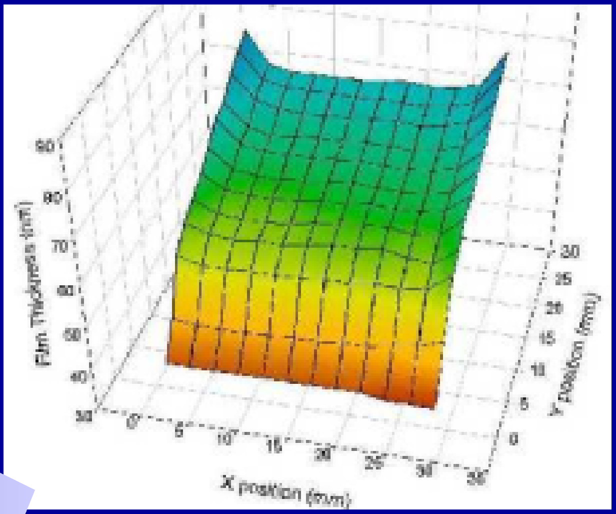
Gradient Film Thickness Library







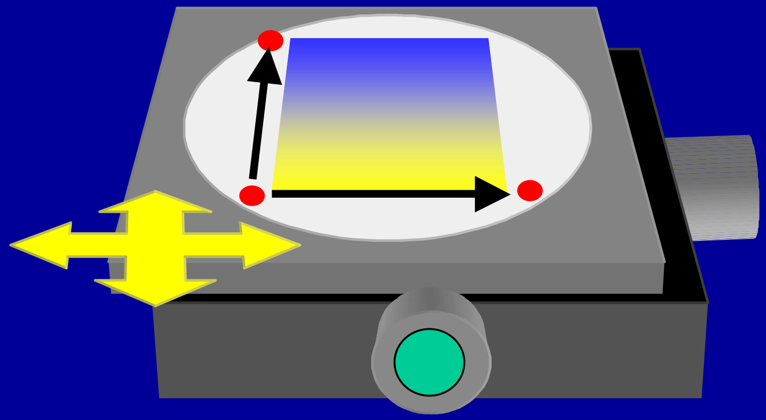
- Thickness calibration mesh is built from point measurements over SRG
- Interpolation allows thickness to be determined anywhere in the library

SRG Pointers:

- Use xy-stages to define reference vectors
  - let calibrated stages work for you

Program automation tools to work within reference system

  - Alignment with reference system should always be the first step of automated analysis



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Notes on Fiduciary Marks:

- Fiduciary marks may be within library borders
  - allows for easy library transfer
- Factors to consider when choosing fiduciary marks:
  - Permanence
  - Readily identified/recognized?
  - Size
  - Calibration measurement technique (ellipsometry? OM?)

Mask Alignment Marks

Lithographic Features

Substrate Flaws

Wafer Flat

Scribe Marks

Library Corners

Library Flaws (e.g. dust particles)

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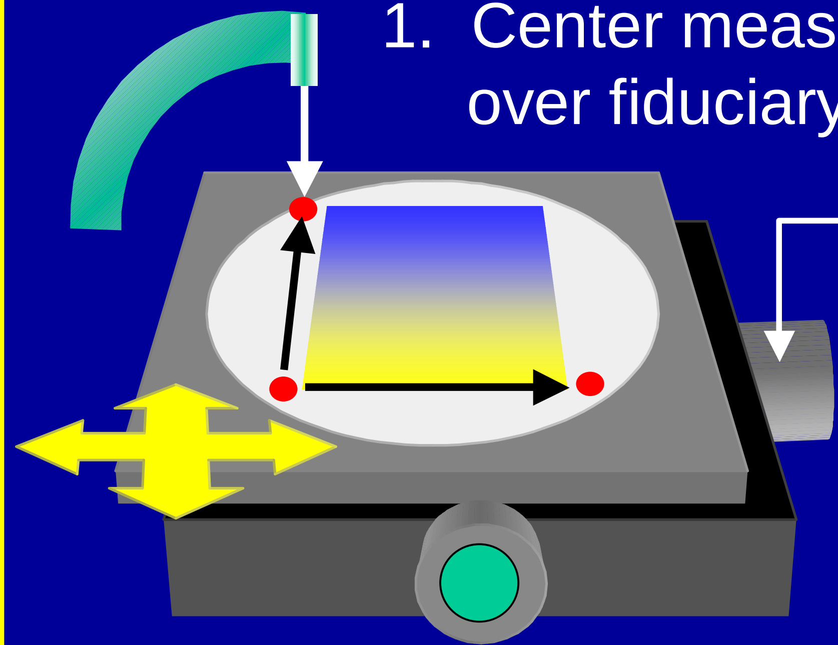
xy-stages and the SRG :

Translation stages with *encoded stepper motors* provide a convenient means of SRG definition



1. Center measurement tool (here interferometer) over fiduciary mark using stage motors
2. Record motor positions
3. Repeat for each mark
4. Define reference vectors
5. Take calibration measurements on grid defined by reference vectors

SRG and Sources of Error

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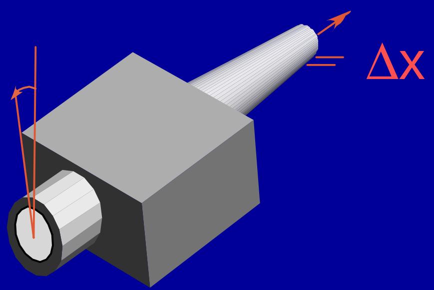
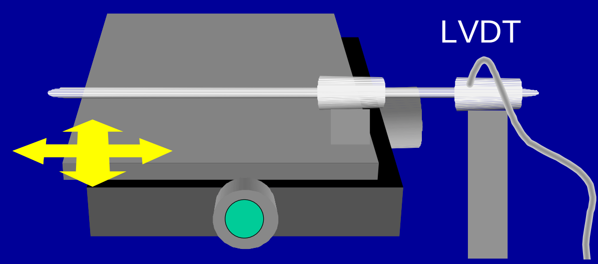
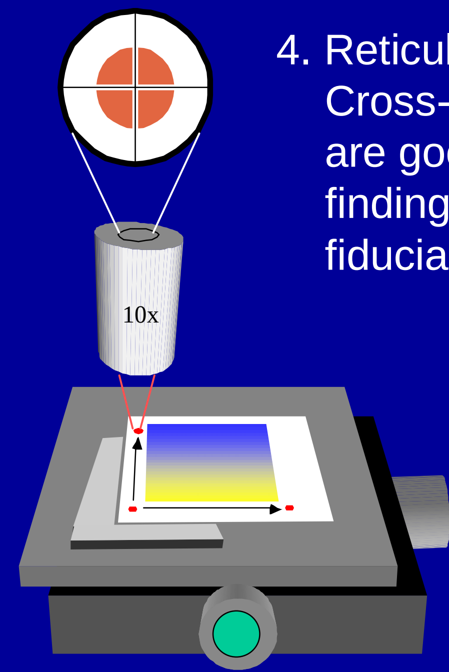
1. Motor step size
2. Stage following error
3. Sample Alignment
4. Fiduciary Mark Registration

} From manufacturer

Solutions:







4. Reticule / Cross-Hairs are good for finding fiduciaries

1. Motor step size: Should be < 5% of measurement footprint

2. Stage following Error:
   - Tune motors properly
   - External fixed encoders to accurately determine position

3. Sample Alignment: Jig/Slot for reproducible sample placement

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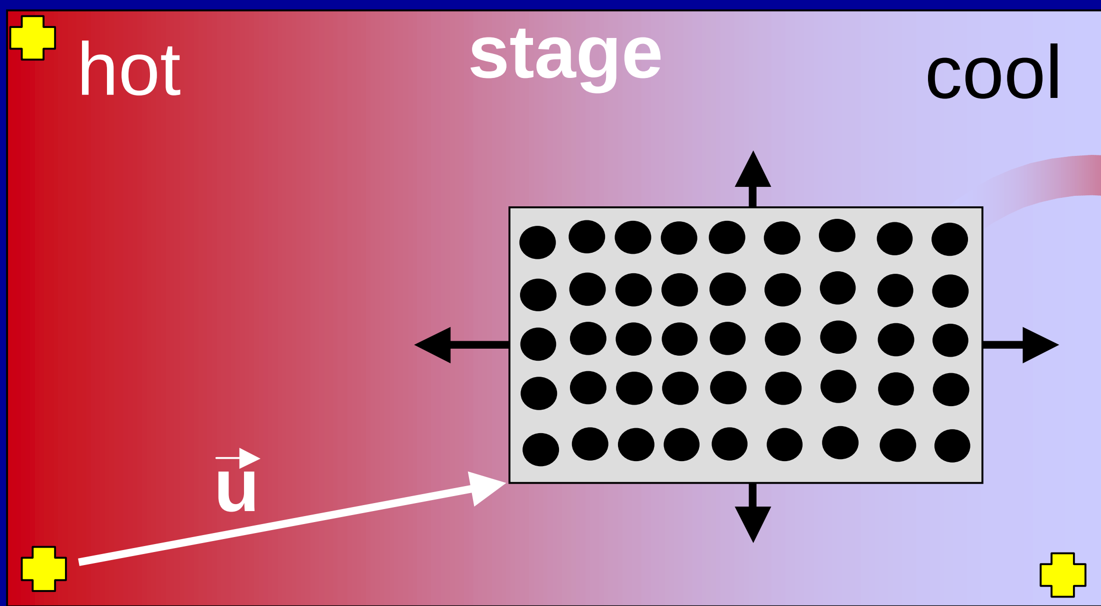
Calibrating Temperature Gradients



Moveable array of T-couples mounted on *application substrate* (e.g. silicon wafer)

- Thermocouple positions mapped first
- Array position ($\vec{\mathbf{u}}$) recorded w.r.t. stage fiduciary marks ✚
- Temperature recorded for each T-couple vs. $\vec{\mathbf{u}}$

Fine mesh of temperature measurements *FAST*

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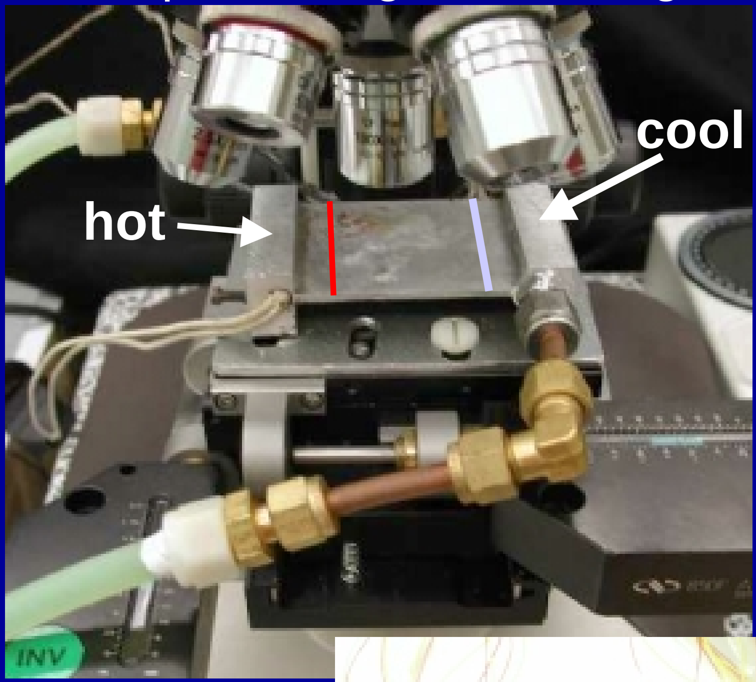
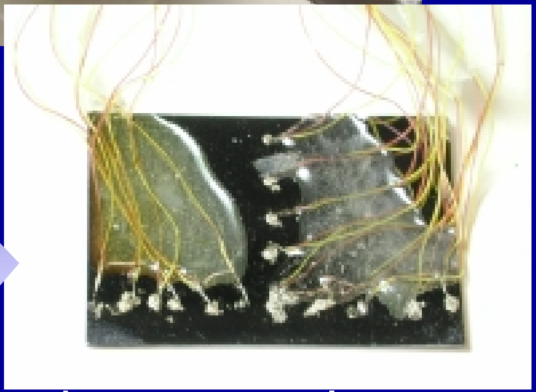
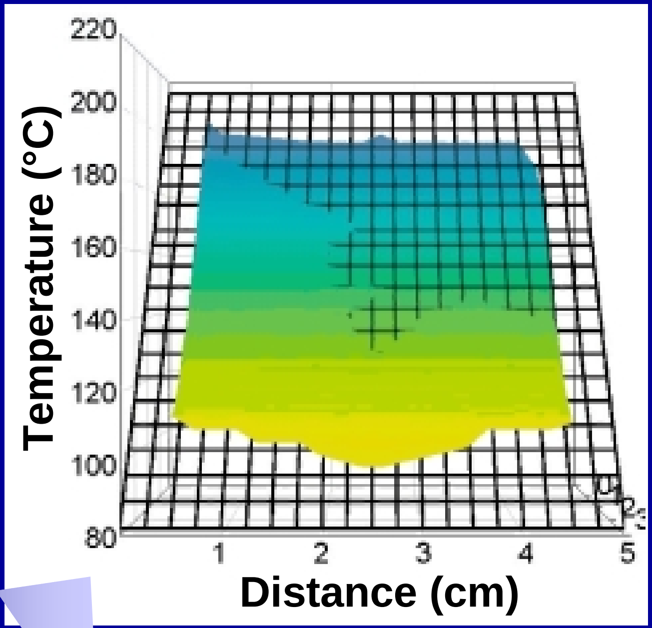
Calibrating Temperature Gradients

Temperature gradient stage





Thermocouple array



Temperature Stage Calibration Surface

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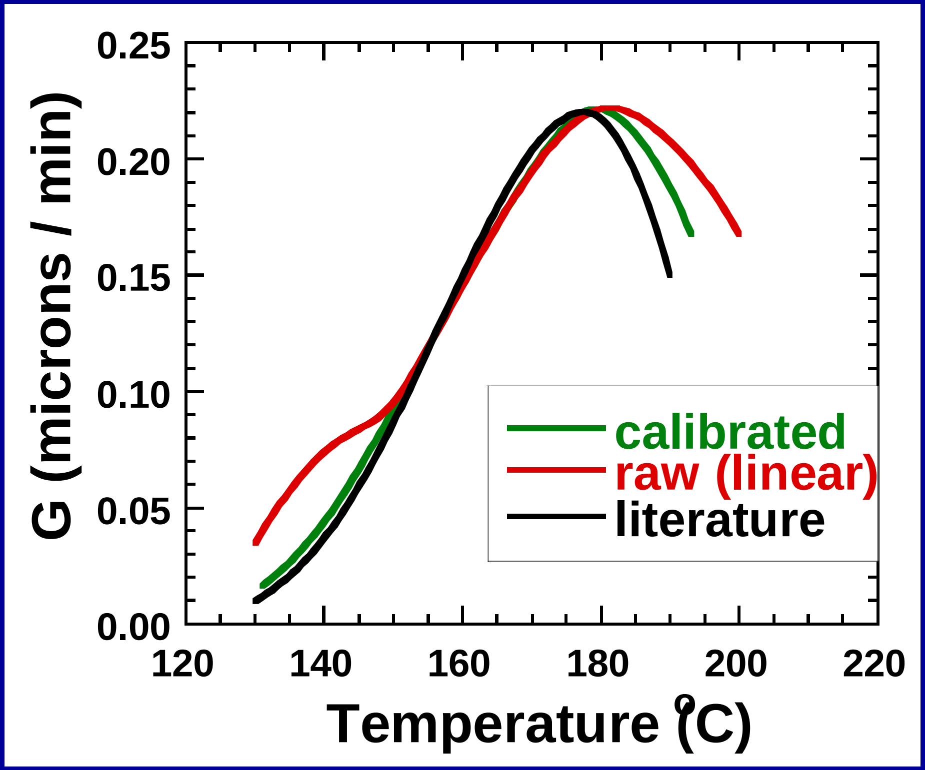
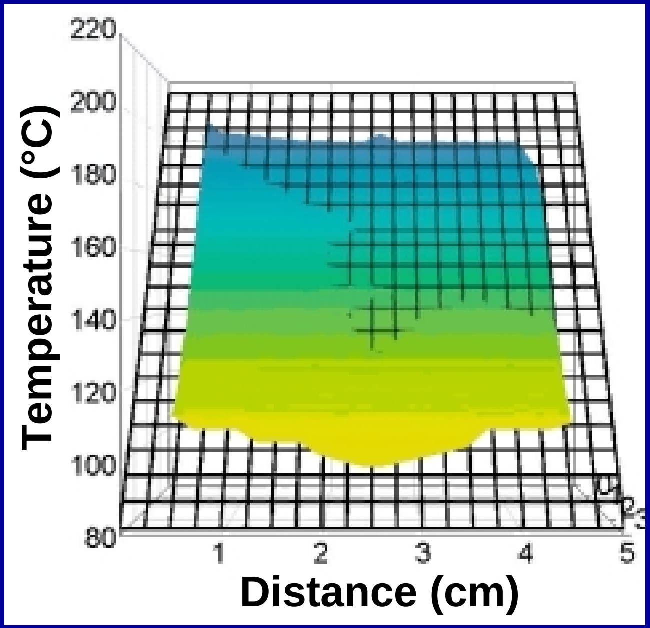
Calibrating Temperature Gradients

Calibration Pays Off





Combi i-PS spherulite growth rate (G) data

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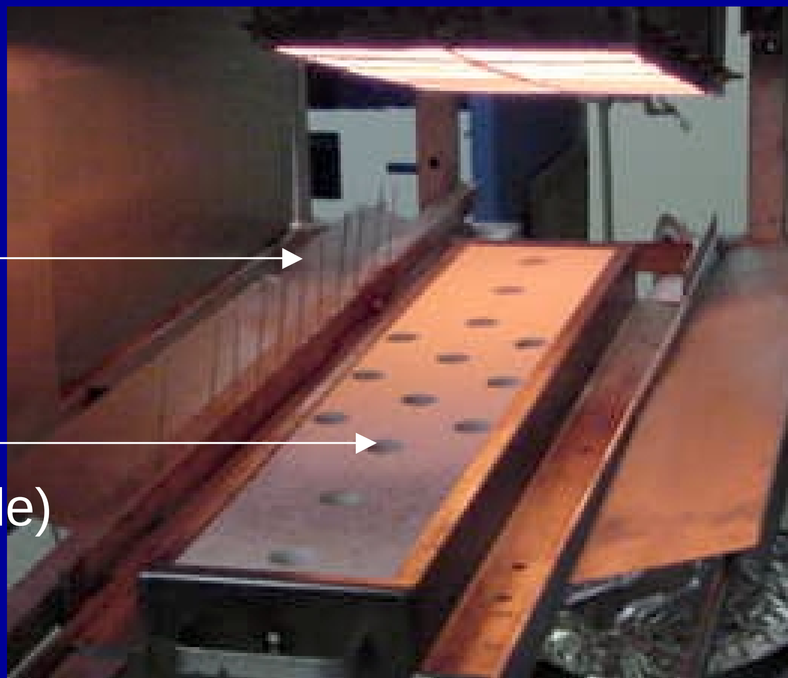
Temperature Gradients
(R. Davis, J. Gilman: BFRL)

Flammability test of extruded plastics

- Pre-load calibration of radiation panel:
  - using flux gauges on sample stage

Flame travel guides

Flux gauge (thermocouple) mounts



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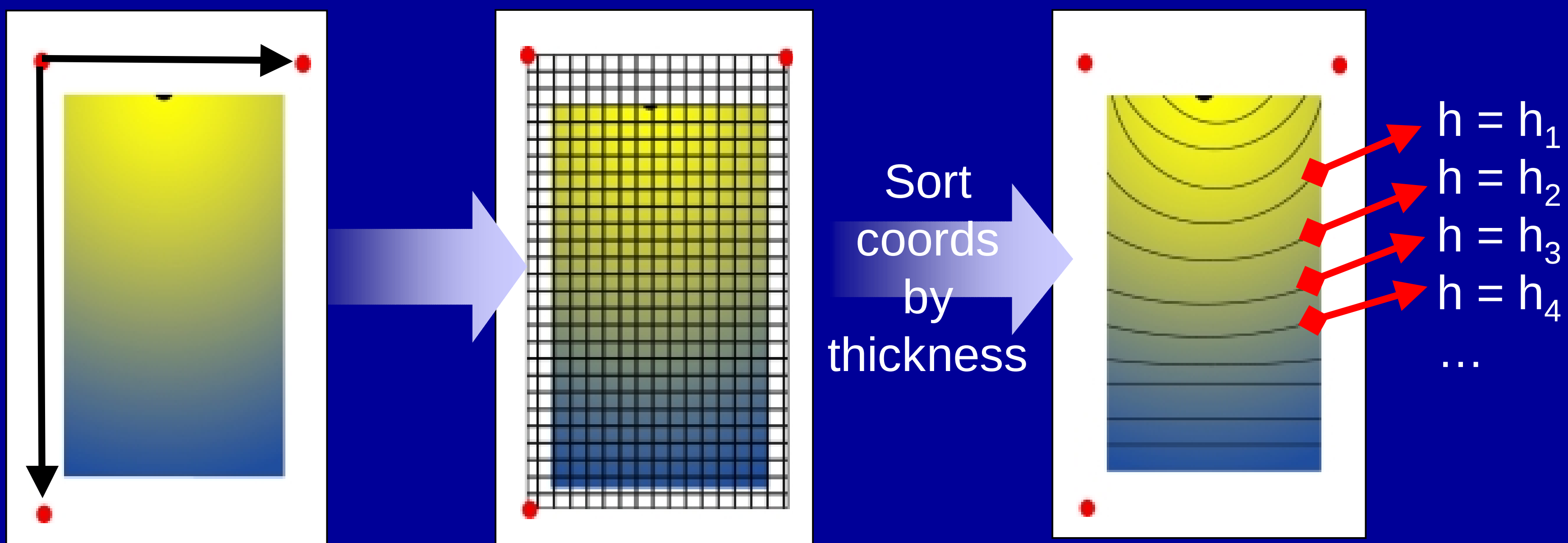
Iso-parametric Contour Lines:

Non-linear spatial distribution → Linear parameter space



Non-linear thickness gradient

Thickness measurements on SRG

Contours delineate coordinates with equal thickness

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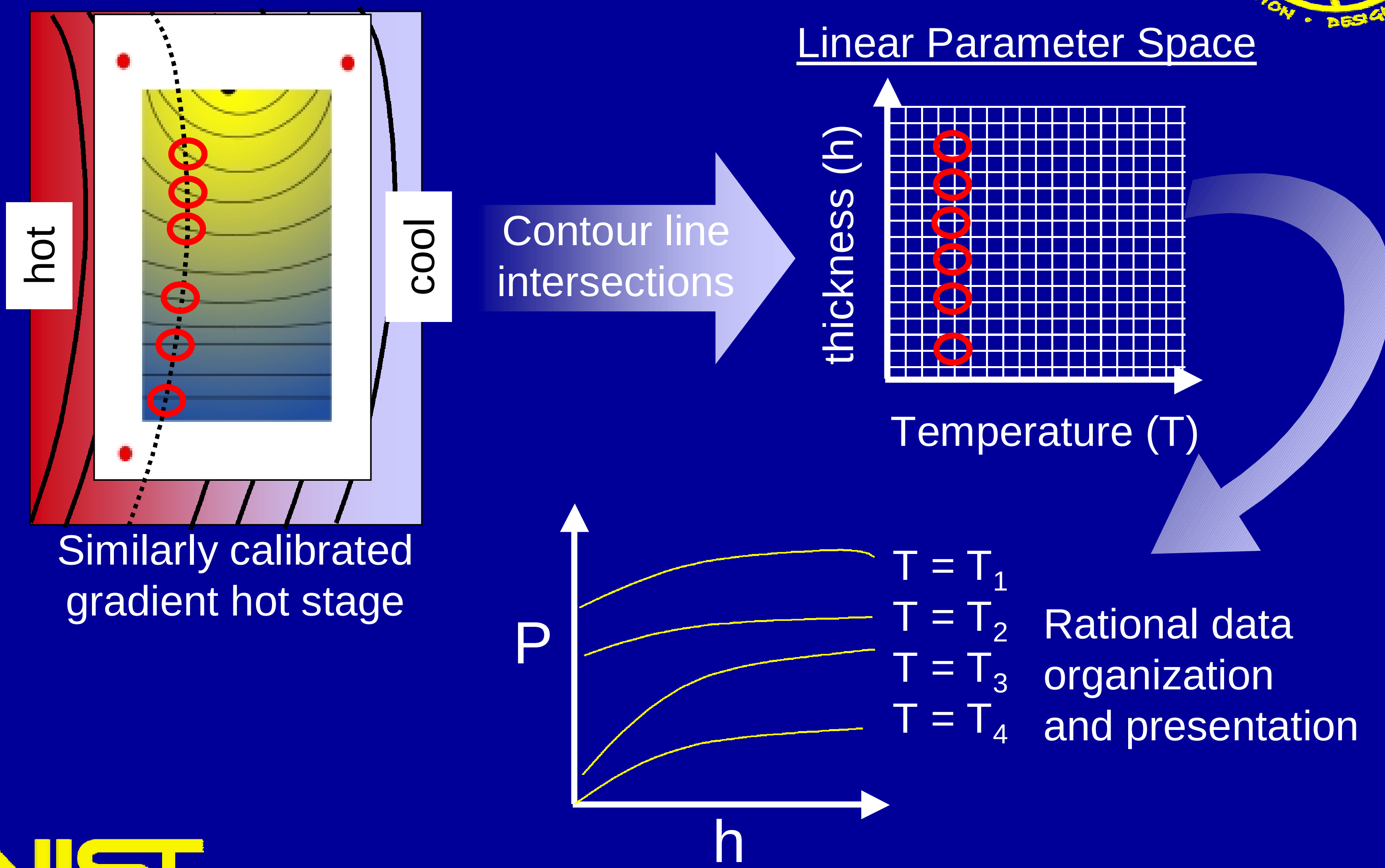
Iso-parametric Contour Lines:

Deconvolution of crossed non-linear gradients



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Utility of Contour Lines:

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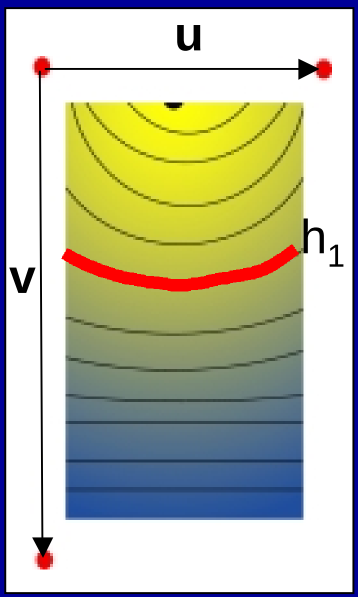
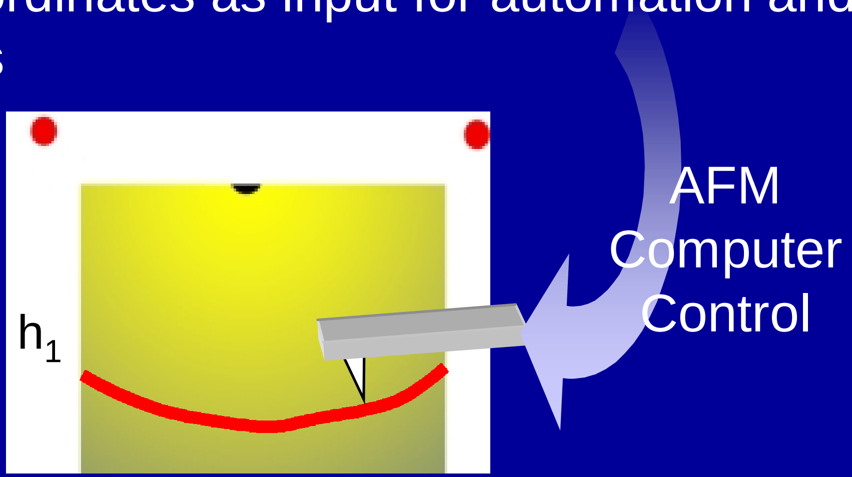
Problem: Thickness "h_1" is of particular interest. How can we concentrate further analysis on this thickness?



Solution:

1) Generate iso-h contours using SRG and calibration mesh
2) Use h_1 contour line to generate coordinates (u,v) for which the thickness equals h_1
3) Use h_1 coordinates as input for automation and informatics



Library Flaws and Defects:

Saving Time!

- Practically all gradient libraries will have defects:
  - E.g. Dust, Scratches
- **Problem:** Does *defect density* negate library?
- **Solution:** Perform a random sampling within library to estimate defect density *before* other characterization steps.

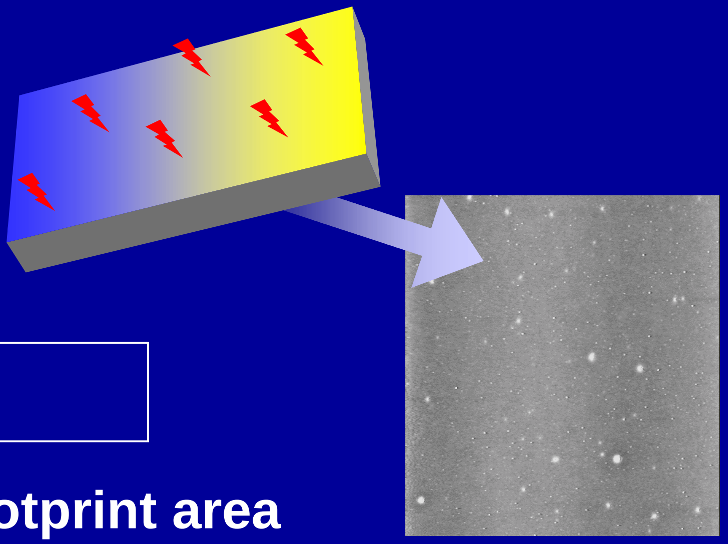
Process:

1. Perform N (10-15) measurements at random places in the library (e.g. micrographs with area A).
2. Count total number of defects: N_D
3. Defect density ≈ $N_D/N \bullet A$

Library rejection criteria:

$$\boxed{\textbf{Defect Density} > 1/A_{CF}}$$

A_{CF}= Characterization method footprint area



Dust / Dirt

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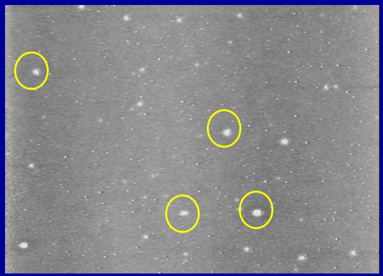
Library Flaws and Defects:

Saving Time!

Example: Is my polymer film clean enough?

- Pick N =10 random points across polymer film library
- Collect optical micrographs with dimension 200 X 500 μm
  - A=100000 μm^2
- Count defects in each micrograph:
  - e.g. total N_D=1000
- Defect Density ≈ 0.001/μm^2
  - 1 defect/1000 μm^2
- Consider Characterization method footprint area
  - e.g. 50 X 50 μm AFM scans: A_{CF} = 2500 μm^2



Defect Density > 1/A_{CF}?
YES: 0.001 > 0.0004 (we expect 2.5 defects/scan)

Conclusion: NOT clean enough, reject library

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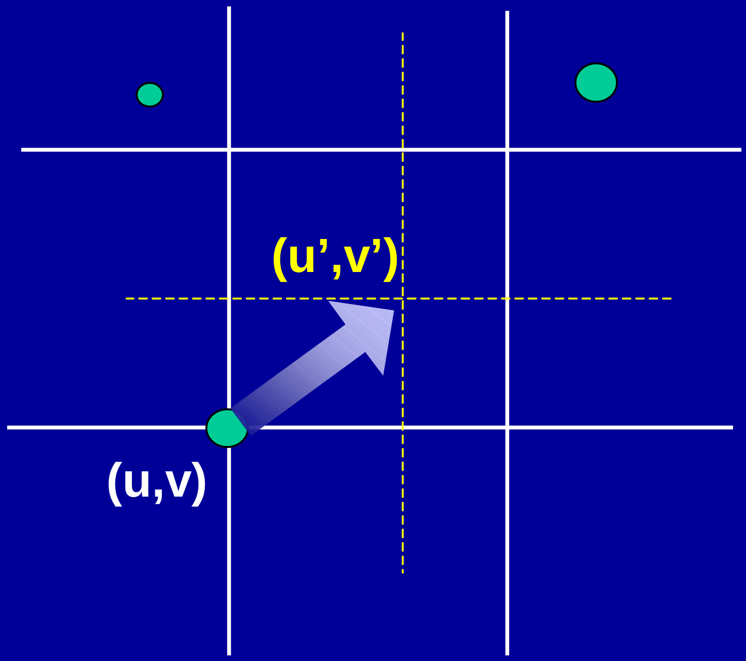
Library Flaws and Defects:

Proper library calibration helps minimize effect of sparse or clustered defects:

Mesh of calibration measurements on spatial reference grid allows for interpolation, which in turn allow for defects to be "skipped over"



Problem: While taking AFM measurements across SRG, a defect is noticed at point (u,v).

Solution: Take measurement at nearby (u',v').

Interpolate library properties at (u',v') using calibration measurements on surrounding points.

= defects

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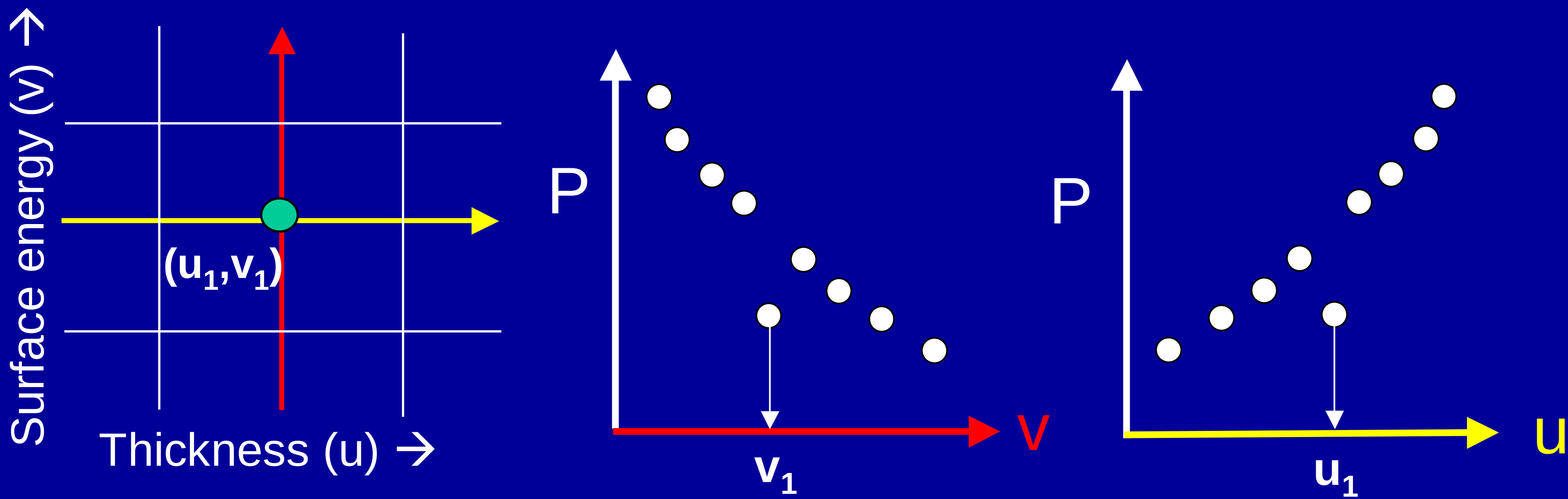
Library Flaws and Defects:

Proper library calibration illuminates “outliers”:
Automatic statistical defect rejection!

Problem: Automated measurement of property **P** over surface energy/thickness grid with a defect at (u_1,v_1).



Solution: Spurious points in P vs. v and P vs. u plots gives *twofold indication* of defect position. This point should be discarded!

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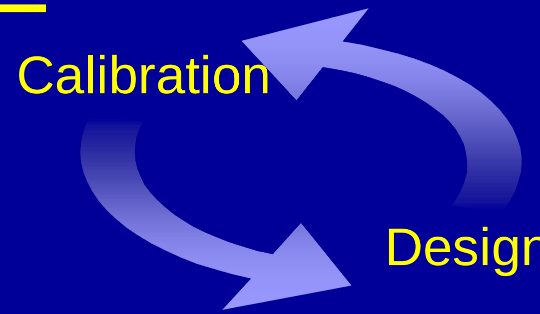
Facilitating library calibration through“Built-in” Standards:



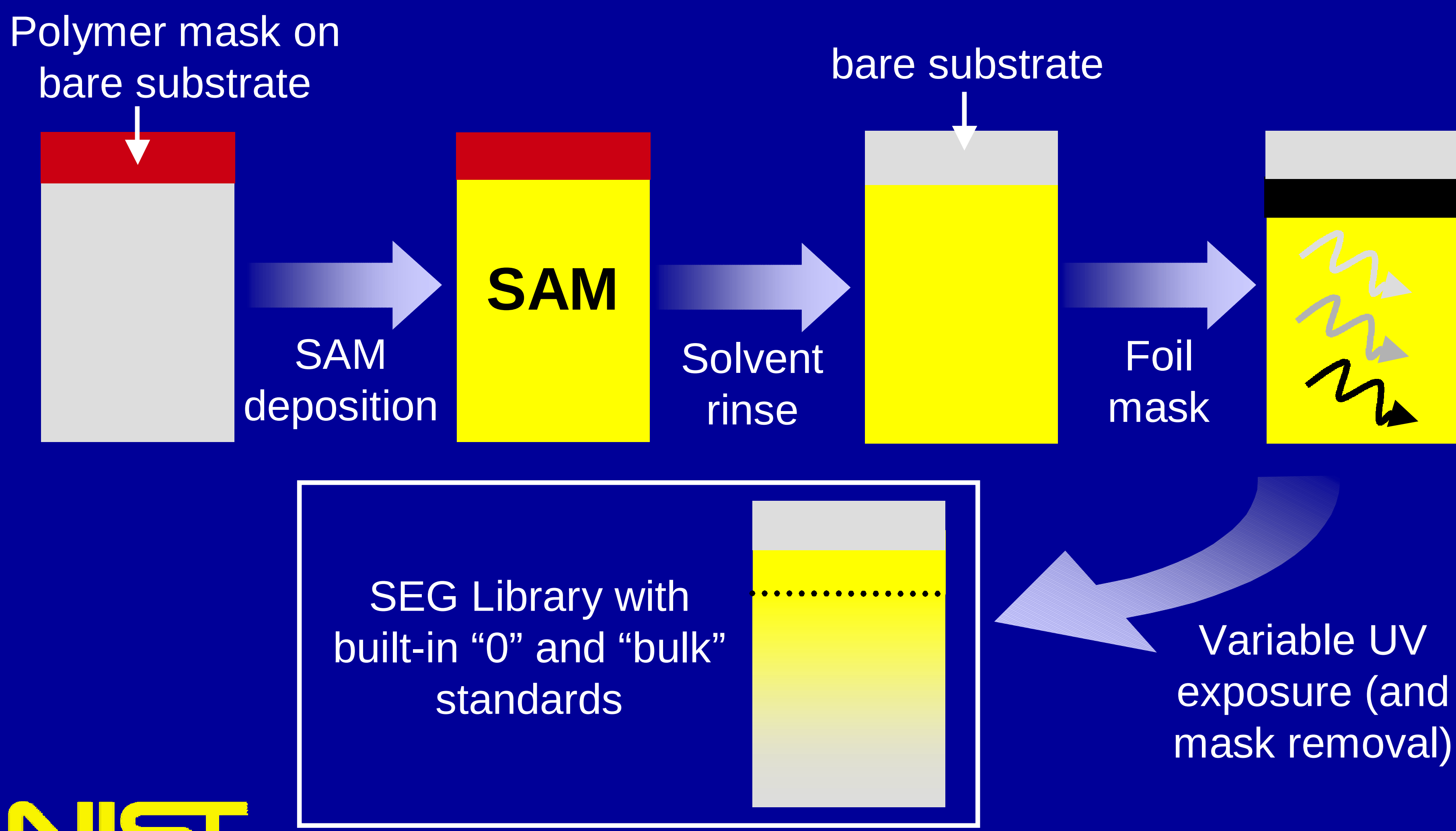
Design library scope to overlap with “known” reference points

Gradient	Built in Standard
Thickness	Bare Substrate “0” or region of “bulk” sample
Composition	100% of one component “Known” composition
Surface Energy	Unmodified substrate Unexposed SAM “Fully Exposed” SAM

Built in Standards “travel” with library through further processing

“Built-in” Standards Example:

UV-generated Surface Energy Gradient



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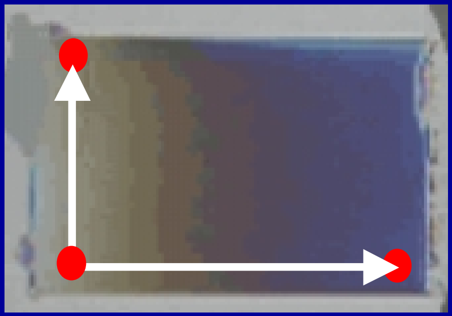
Library Transfer

Calibration

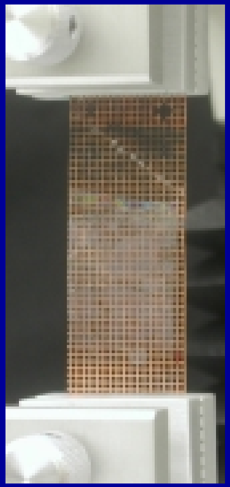
Design

Problem: Combi experiment requires mounting library on a substrate that is not amenable to film casting.

- Copper Grid
- Flexible PDMS



Cast on silicon wafer or glass



Copper Grid

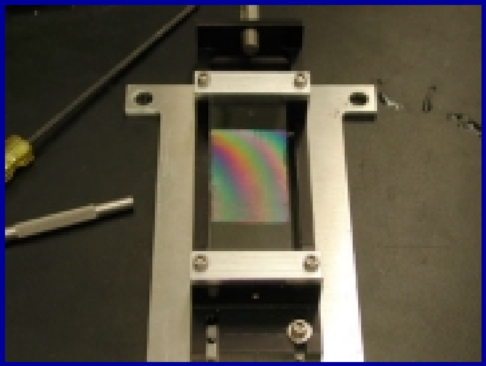
Solution:

1) Cast film on appropriate substrate.

2) Establish spatial reference grid *within the library borders*

3) Transfer library (e.g. float)

Reference "travels" with library



PDMS substrate

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Resolution, Uncertainty, Tolerance

- How many characterization measurements should be made over a library?
  - SRG spacing or “resolution”
  - Characterization technique footprint
  - Gradient steepness

- What will be the error of my characterization measurements?
  - Local Gradient
  - Characterization technique footprint

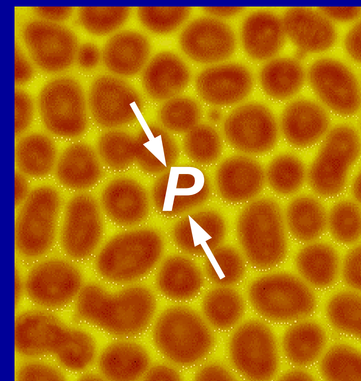
Resolution, Uncertainty, Tolerance

Calibration

Design

Example : Phase Separated Blend Morphology

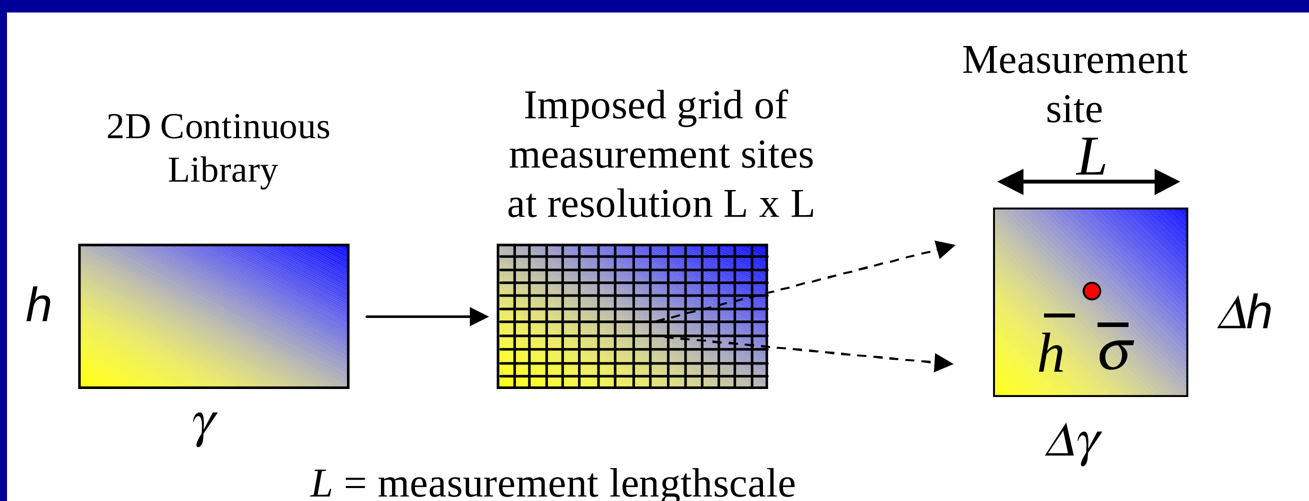
- P = phase domain width: P=f(γ,h)
- Continuous gradients cause variance in observed property P



Δ *Thickness* (*h*)

Δ *Surface Energy* (γ)

- Lateral resolution (L) affects variance



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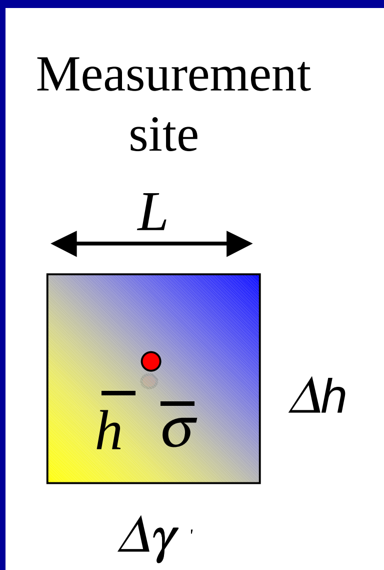
Uncertainty: Gradients & Resolution

Standard uncertainty propagation

Carson Meredith

$$\Delta\langle P\rangle = (\partial\langle P\rangle/\partial N)\,\Delta N + (\partial\langle P\rangle/\partial h)\,\Delta h + (\partial\langle P\rangle/\partial \sigma)\,\Delta\sigma$$



An optimization problem:

L ~ Measurement footprint dimension

microscopy: Optical, AFM, Fluor., FTIR

spectroscopy: IR, UV

- '*ΔThickness*' and '*ΔSurface Energy*' are minimized with ↓ *L*
- *N* ~ Number of microstructural features to be measured over footprint

N ~ L^2 (Area of micrograph)

statistics better as L↑

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Uncertainty/Library Optimization

$$\Delta\langle P\rangle = (\partial\langle P\rangle/\partial N)\,\Delta N + (\partial\langle P\rangle/\partial h)\,\Delta h + (\partial\langle P\rangle/\partial \sigma)\,\Delta\sigma$$

An Iterative Process:

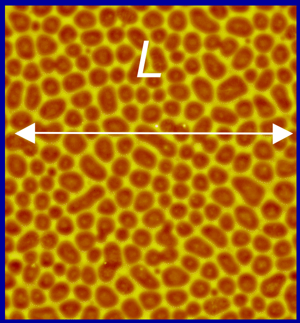
Step 1 - Define Footprint Size *(L)* :

Good Statistics: N ~100

Estimate: Max. domain size *(P)* ~ 6 μm

$L \sim \sqrt{N} \times P \sim 60\ \mu m$

$(\partial\langle P\rangle/\partial N)\,\Delta N \sim \langle P\rangle.(\Delta N/N) \sim 0.01\langle P\rangle$



Δh

$\Delta\gamma$

Step 2 - Initial estimate of Acceptable Gradients

Conservative: Thickness $\Delta h = 0.1$ nm

Surface energy $\Delta\gamma = 0.1$ mJ m^{-2}

For a 3 cm × 3 cm area Library:

$\Sigma\,\Delta h = 50\ nm$ $\Sigma\,\Delta\gamma = 50\ mJ\ m^{-2}$ (Library scope)

Step 3 - Create Library with Acceptable gradients

$\Sigma\,\Delta h < 50\ nm$ $\Sigma\,\Delta\gamma < 50\ mJ\ m^{-2}$ (Library scope)

e.g. $\Delta h = 0.06\ nm$ $\Delta\gamma = 0.06\ mJ\ m^{-2}$ (Average slope)

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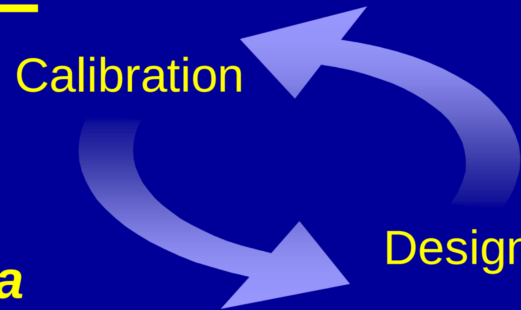
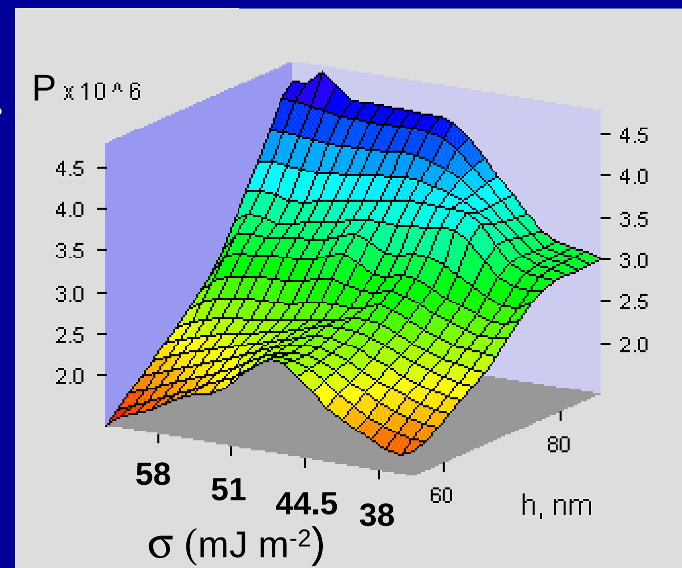
Uncertainty/Library Optimization



Step 4 – Go to Library: Measure Max Slopes in Data

$(\partial \langle P\rangle/\partial \gamma)_{max} = 0.2\ \mu m/(mJ\ m^{-2})$

$(\partial \langle P\rangle/\partial h)_{max} = 0.1\ \mu m/(nm)$



Step 5 – Estimate Max Error ($\Delta\langle P\rangle$)

$$= (\partial \langle P\rangle/\partial N)\,\Delta N + (\partial \langle P\rangle/\partial h)\,\Delta h$$

$$+ (\partial \langle P\rangle/\partial \sigma)\,\Delta\gamma$$

$$= 0.01\langle P\rangle + 0.1 \times 0.06 + 0.2 \times 0.06$$

$$\Delta\langle P\rangle = 0.01\langle P\rangle\ \mu m + 0.018\ \mu m$$

For <P>=1.5 microns (smallest measured domain) → 2.2% error

Step 6 – Adjust Gradients to meet apriori criteria keeping the same L

e.g $\Delta\langle P\rangle < 1\%$ → ***Design Input, go to step 2***

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A combinatorial database from gradient libraries

- Screen libraries to reduce contributions from flawed data points
  - Use developing knowledge to optimize fabrication methods on *successive iterations*
- Create the appropriate spatial reference grids to discretize subregions of the library
  - Use developing knowledge to optimize variable space and measurement ranges on *successive iterations*
- Validate libraries with “built in” standards
  - Use discrete samples and existing knowledge (literature) to begin in new areas
- Use scope and tolerance to validate measurements and determine uncertainty
  - feedback from *each cycle* can simultaneously facilitate automation and reduce uncertainty

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